APPENDIX "K"

11/29/94
Emission Estimation Methodologies[1]

The methodologies presented in this attachment are based on the Ideal Gas Law and on fundamental vapor/liquid equilibrium relationships such as Henry's and Raoult's Law, unless otherwise specified. The equations are intended for use in estimating and characterizing uncontrolled emission streams from batch processes. Example calculations are presented for several unit operations. Significant errors may result in using the examples for situations that do not meet the conditions and/or assumptions that are clearly stated in the presentation of the methodologies.

a.   Process Vent Emissions

Process vent emissions may result from a number of different events. Common process vents in batch processing result from drying, tank and reactor inert gas purging, vapor displacement losses from material transfer, tank and reactor heating, gas evolution, gas sparging, batch pressure filtration, and vacuum generation. The discussion below presents the principles and methodologies for estimating emissions during these events.

1.   Drying

Two types of drying operations commonly occur in batch processing. These are conductive drying, in which heat is transmitted to the material to be dried by contact with heated surfaces, and convective drying, in which heat is transmitted by hot gases which are in contact with the material. Conductive drying may occur under vacuum conditions or at atmospheric pressure and in several types of dryers, including tray dryers, tumble (double-cone) dryers, pan dryers, and rotary dryers. Convective drying occurs at atmospheric pressure. Convective dryers include rotary dryers, fluid bed dryers, and spray dryers.

The methodology for calculating emissions from the types of dryers described above is essentially the same. In general, the rate of drying of the material depends on many factors associated with the specific drying situation (i.e., moisture or solvent content of material to be dried, heat and mass transfer parameters, drying period, etc.), but generally decreases with time so that a large percentage of the total liquid will be removed during the beginning of the drying cycle.

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[1]Material in this Appendix has been derived from guidance in Chapter 3 and Appendix C of EPA's draft CTG for Batch Processes (EPA-453/R-93-017).

Studies on the theory of solids drying usually relate drying rate to moisture content of the solid. Three distinct periods of drying can be observed: the constant-rate period when surface moisture is evaporated; the funicular state when capillarity of the liquid in the pores influences the drying rate; and the pendular state when capillary action ceases and the liquid must diffuse through the pores of the solid. Each of these three drying periods has successively lower rates of drying; the final drying rate, when the moisture content is zero, is of course also zero.[1]

Dryer designers often generate drying curves expressing the rate of drying as a function of residence time. Laboratory or pilot-scale experiments are often needed to establish the correct dryer size, operating temperature, gas flow rate, and cycle time. Once a dryer is installed and operating, readily available data include the cycle time, gas flow rates, and moisture content of the solid at the start and finish of the cycle. If very dry solids are produced (i.e., zero moisture content), the drying rate at the end of the cycle will be asymptotic to zero. This end point condition, and a knowledge of the total solvent removed, can be used to estimate the emission characteristics of an existing, installed dryer.

In industrial practice, the filter cakes and centrifuged solids to be dried often appear dry and free-flowing and may contain up to 50 percent solvent by weight. At the end of the drying cycle, the solvent content is reduced to a level required by the process. From a mass balance, the total amount of solvent emitted can be calculated.

To properly size emission control equipment for dryers, however, one must know the exhaust stream VOC content throughout the cycle. Although the precise VOC content can only be determined from extensive laboratory testing, a reasonable estimate can be obtained by assuming that the rate at which the drying rate decreases is linear over the length of the drying cycle starting from the initial, highest value and declining to zero at the end of the cycle. From the material balance on solvent removed, the average drying rate can be calculated knowing the length of the cycle. With a straight line relationship and a final value of zero, the initial drying rate must be two times the average. Therefore, the drying rate, and hence the emission rate, can be estimated for any point in the drying cycle.

      i.   Vacuum Dryers. Tray dryers, double-cone dryers, pan dryers, and rotary dryers may be operated under vacuum conditions. Such vacuum dryers will have an inward leakage rate of air that will aid in transporting the VOC's and air toxics that have evaporated from the dryer's product. Vacuums in the range of 15 to 25 inches mercury are typical. Articles have been

published which provide methods of estimating leakage rates for vacuum systems.[2] One such methodology is contained in Section 8 of this Appendix. For a single dryer, the air leakage may range from 10 to 30 scfm depending on system design and vacuum level desired. An example calculation of vacuum dryer emissions follows:

Example: Consider the following example of a double-cone dryer operating at 15 inches of mercury, with an air-leakage rate of 15 scfm. The temperature inside the dryer is 60°F. Three hundred pounds of product cake, initially containing 25 percent by weight acetone are dried to less than 1 wt% solvent over the course of 8 hours. Calculate the maximum VOC emission rate.

Solution. The total amount of acetone dried from the product cake is:

$$\frac{300 \text{ lb cake}}{} \mid \frac{0.25 \text{ lb acetone}}{\text{lb cake}} = 75 \text{ lb acetone (initially)}$$

$$\therefore 300 - 75 = 225 \text{ lb product in cake}$$

The amount of acetone remaining at the end of the cycle is:

$$\frac{x}{225 + x} = 0.01$$

$$x = (0.01 (225 + x)$$

$$x = 2.25 * 0.01x$$

$$0.99x = 2.25$$

$$x = 2.3 \text{ lb acetone (at end of cycle)}$$

Therefore, the total amount of acetone removed from the drying cycle is:

$$75 - 2.3 = 72.7 \sim \underline{73 \text{ lb}}$$

Average emission rate over the drying cycle is:

$$(73 \text{ lb/8 h}) \ (1 \text{ h/60 min}) = 0.15 \text{ lb/min}$$

The initial drying rate is two times the average rate, assuming a straight-line decline.

Maximum (initial drying rate)

$$(2) \times (0.15) = 0.30 \text{ lb/min}$$

MW acetone = 58 lb/lbmol

Therefore, the molar flow of acetone is:

$$(0.30 \text{ lb/min}) \ (\text{lbmol/58 lb}) \ (60 \text{ min/hr}) = 0.31 \text{ lbmol/h}$$

The airflow (leakage) is given as 15 scfm where 359 scf (at 0°C and 1 atm) is 1 mole. Therefore, the molar flow rate is:

$$(15 \text{ scf/min}) \ (\text{lbmol/359 scf}) \ (60 \text{ min/h}) = 2.51 \text{ lbmol/h}$$

Therefore, the uncontrolled emission stream properties at the start of the drying cycle are estimated to be:

Component	lbmol/h	mole fraction
Acetone	0.31	0.110
Air	2.51	0.890
TOTAL	**2.82**	**1.000**

The 0.31 lbmol/hr rate represents the maximum VOC emission rate during the cycle.

ii.   Atmospheric Dryers. Convective dryers, such as tray and fluid bed dryers, operate at or above atmospheric pressure. The four types of conductive dryers discussed previously, tray dryers, double-cone dryers, pan dryers and rotary dryers may

also be operated at atmospheric conditions. A stream of air or inert gas is used to move the volatilized material from the dryer vessel in conductive drying. The gas stream serves as the heating mechanism in convective drying. In both of these situations, the calculation of total VOC content emitted during the drying cycle is identical to the vacuum drying method (i.e., a mass balance from initial cake concentration to final cake concentration). The estimation of the maximum dryer emission rate, which is used for sizing of equipment, is analogous to the method presented for vacuum drying, with the flow rate of gas through the system equal to the dryer exhaust gas rate. An example calculation of atmospheric dryer emissions follows:

Example: A tray dryer uses 6,000 acfm of heated air (65°C) over a period of 6 hours to remove isopropyl alcohol (IPA) from a batch of solids. Each batch consists of 1,000 pounds of material containing 40 percent (by weight) solvent. The final product contains less than 0.6 percent solvent. Calculate the total uncontrolled VOC emissions per drying cycle and the maximum VOC emissions rate.

Solution: Mass balance over the drying cycle:

$$(1,000 \text{ lb cake}) (0.40 \text{ lb IPA/lb cake}) = 400 \text{ lb IPA initially}$$

$$\text{Quantity of bone-dry solids} = 1,000 - 400 = 600 \text{ lb}$$

Amount of IPA remaining:

$$\frac{x}{600 + x} = 0.006$$

$$\therefore x = 3.6 \text{ lb IPA}$$

Amount of IPA removed is:

$$400 - 3.6 = 396 \text{ lb} \qquad (MW = 60.09)$$

$$\text{Average emission rate} = 396 \text{ lb/6 h} = 66 \text{ lb/h}$$

$$\text{Assume initial rate} = 2 \times \text{average rate}$$

$$(2) (66) = 132 \text{ lb/h}$$

$$(132 \text{ lb/h}) (\text{lbmol/60.09 lb}) = 2.20 \text{ lbmol/h}$$

Calculate composition of uncontrolled emission stream at start of drying cycle:

Airflow:
(6,000 acf/min) (60 min/h) (lbmol/359 scf) (273/273+65)scf/acf = 810 lbmol/hr

Component	lbmol/h	mole fraction
IPA	2.20	0.0027
Air	810	0.9973
TOTAL	**812.2**	**1.0000**

Knowledge of, or an estimate of (as above), the uncontrolled outlet stream composition is necessary to select an appropriate control technology. One should note that the mole fraction of the VOC is considerably lower (approximately two orders of magnitude) in the convective oven exhaust than in the vacuum oven (previous example).

2. Tank and Reactor Purging

In batch processing a gas stream is frequently used to purge VOC vapors from either an empty tank or reactor vessel, or from the vapor space of a partially filled tank or reactor. Typical reasons for purging are to maintain product quality (e.g., by using a dry sweep gas to minimize water vapor in a system) or to dilute flammable vapor concentrations below safety limits.

i. Empty Tank Purging. Empty vessels may be purged intermittently (e.g., at startup and shutdown, or between batches) using a displacement purge to remove accumulated vapors. The estimation of VOC emissions in this case is fairly straightforward. Before the purge, the initial VOC concentration of an empty vessel's vapor space is assumed to be equivalent to vapor in equilibrium with the removed liquid.

The final concentration is a function of the number of purge gas volumes used. This relation can be expressed as a power law:

$$\frac{C_f}{C_i} = x^n \qquad (1)$$

where:

    n   =   the number of purge gas volumes used;
    x   =   the fractional dilution per volume change;
    C_f =   final concentration in vessel; and
    C_i =   initial concentration in vessel.

The fractional dilution per volume change assuming perfect mixing has been shown to be 37 percent. Thus, equation 1 becomes:

$$\frac{C_f}{C_i} = (0.37)^n \qquad (2)$$

This equation does not account for evaporation of any residual liquid in the vessel, and no free liquid. The equation was derived via the following steps:

$$\frac{d(VC_a)}{dt} = -qC_a \qquad (3)$$

where:

    V   =   vessel volume
    C_a =   concentration of VOC species
    q   =   volumetric purge rate
    t   =   time

if: $q = 1$ ft^3/min and $V = 1$ ft^3, then equation (3) reduces to:

$$\frac{dC_a}{C_a} = -dt \qquad (4)$$

By integrating and setting the following boundary limits:

$$t = 0 \qquad\qquad C_a = C_i$$
$$t = 1 \qquad\qquad C_a = C_f,$$

then equation (4) reduces to

$$\ln (C_f/C_i) = -1 \tag{5}$$

Therefore, $C_f = 0.37 C_i$

Emissions are calculated by multiplying the vessel volume by the difference between final and initial concentrations, $(C_f - C_i)$.

ii.   Filled Vessels. Filled or partially filled vessels are often "blanketed" with inert gas (or even air in the case of nonflammable solvents) using either "balanced pressure" or "trickle" control schemes[3]. With balanced pressure blanketing, there is no flow of gas unless the tank liquid level changes (during filling or emptying) or the pressure rises or falls due to thermal effects. The calculation of emissions from this type of blanketing is analogous to "working and breathing" losses. For trickle blanketing, a constant flow of gas is maintained through headspace. The flow rate may be quite low for a storage tank, but may be much higher for a reactor where removal of water vapor or excess solvent vapor is required. The higher flows are referred to as purges or sweeps.

The volatile organic content of a purge gas stream may be calculated by assuming that the gas is saturated with the vapors of the liquid over which it is flowing. This assumption is generally conservative in that the VOC content of a gas cannot possibly be greater than saturation concentrations (as long as there are no entrained droplets). To calculate a maximum expected uncontrolled emissions rate, this approach is acceptable. However, the actual VOC concentration of the exiting purge gas may be substantially below saturation. Calculations show that the percent saturation of an inert gas purge stream over a quiescent pool of liquid is expected to be no more than 10 percent. The purging of equipment with a turbulent liquid surface leads to higher saturation fractions, approaching 100 percent saturation at lower flowrates. Since most vessels are typically agitated, the conservative assumption of complete VOC saturation is recommended at low to moderate purge gas flow rates. However, if the purge flow is greater than 100 scfm, a saturation factor of 25 percent is recommended.

Most operations are run at conditions, such as atmospheric pressure and relatively low temperatures, which allow the application of the ideal gas law. The VOC emission rate from purging may be estimated by first calculating the volumetric flow rate of the gas leaving the vessel, consisting of noncondensibles as well as the volatilized VOCs. The total rate of gas exiting a vessel is therefore:

$$Vr_2 = Vr_1 \left[\frac{P_T}{P_T - \Sigma (P_i X_i)} \right] \qquad (6)$$

where:

Vr_2	=	rate of gas displaced from the vessel (VOC and noncondensibles), scfm
Vr_1	=	rate of purge gas (noncondensibles), scfm
P_T	=	vessel pressure, mmHg
$\Sigma(P_i X_i)$	=	the sum of the products of the vapor pressures and mole fractions for each VOC, mmHg

The emission rate of VOCs in this exit gas is then calculated using the following equation:

$$E_R = \frac{(Y_i)\ (V_r)\ (P_T)\ (MW)}{(R)\ (T)} \qquad (7)$$

where:

E_R	=	mass emission rate;
Y_i	=	mole fraction in vapor phase, calculated in Equations (9) and (10) to follow.
V_r	=	volumetric gas displacement rate (equal to the total rate of gas exiting a vessel, Vr_2)
R	=	ideal gas law constant;
T	=	absolute temperature of the vessel vapor space, (°K or °R);
P_T	=	pressure of the vessel vapor space; and
MW	=	molecular weight of the VOC or air toxic.

3. Vapor Displacement Losses--Transfer of Material to Vessels

Emissions occur as a result of vapor displacement in many batch operations. The transfer of liquids from one vessel to another vessel causes a certain volume of gas to be displaced in the receiving vessel. The VOC's that may be contained in this volume also are displaced. In many cases, the displaced gas is vented directly to the atmosphere. The amount of VOC's emitted during such an event is limited by the

partial pressure of the components in the gas stream and the vessel pressure. Usually, vessel vapor spaces are filled with air (i.e., 21 percent oxygen, 79 percent nitrogen) or an inert gas, such as nitrogen.

The degree of vent gas saturation with the VOCs must be assumed or known before any calculations are performed. When permit levels are established, a conservative assumption is typically made to prevent a low estimate of emissions. In most vapor displacement calculations one may conservatively consider the gas being displaced to be 100% saturated with the volatile compounds that are entering the vessel. The following steps are involved in calculating emissions from vapor displacement events:

Step 1. Define the conditions of the displaced gas:

1. Temperature;
2. Pressure; and
3. Volumetric rate of displacement.

The rate of displacement of a gas from a vapor space is equal to the rate of vessel filling with liquid. An example of this displacement is the transfer of liquid material from one process vessel to another, such as the charging of a reactor with material from a weigh tank, and the subsequent emission reactor gas that is saturated with the vaporized liquid.

Step 2. Calculate the mole fraction of components in displaced gas:

The vapor pressure of the compound of interest (for one specific component, such as an air toxic) or of the entire volatile component of the liquid (for total VOC emissions) must first be determined. For one component, this can be done by consulting vapor pressure tables at the appropriate temperature or by using Antoine's equation, a form of which is presented below:

$$\ln P_i^* = A - \left[\frac{B}{(T + C)} \right] \tag{8}$$

where:

P_i^* = vapor pressure of component i (mmHg);
A, B, C = compound-specific constants; and
T = absolute temperature of the liquid (K).

There are several forms of vapor pressure estimation equations and the reader should be certain that the constants correspond to the appropriate form and that the units are consistent. Most physical property handbooks contain the Antoine equation and the appropriate constants.

If more than one compound is present in the liquid, the vapor pressure of all compounds in the mixture must be determined. After the vapor pressures have been determined, the partial pressure that the VOC vapor fraction exerts in the vessel vapor space may be determined by using Raoult's Law, which is a simple expression that describes equilibrium between an ideal vapor and an ideal liquid. The general equation for Raoult's Law is presented below:

$$Y_i = \frac{P_i}{P_T} = \frac{X_i P_i^*}{P_T} \qquad (9)$$

where:

Y_i = mole fraction of i in the vapor
P_i = partial pressure of component i;
X_i = mole fraction of component i in the liquid;
P_i^* = vapor pressure of component i at temperature T; and
P_T = the total pressure in the vessel vapor space.

Raoult's Law may be used for multicomponent systems, assuming the compounds are completely miscible in one another. If the compounds are not miscible, or are only partially miscible, then they are considered "nonideal" and Raoult's Law does not apply. At or above the solubility limit, each compound exerts a partial pressure in the vapor space which is equal to the vapor pressure at that temperature. Below the solubility limit, especially for dilute solutions comprised of water and trace amounts of air toxics or VOC's, Henry's Law is used to describe the relationship between the mole fraction of the compound in the liquid and the vapor phase mole fraction. Henry's Law is presented below:

$$Y_i = \frac{P_i}{P_T} = \frac{X_i H_i}{P_T} \qquad (10)$$

where:

X_i = mole fraction of component i in the liquid;
H_i = Henry's Law constant for i (at temperature T);
Y_i = mole fraction of component i in vapor; and
P_T = the total pressure in the vessel vapor space.

This relationship is especially important in calculating evaporative losses from process wastewater.

Step 3. Calculate the emission rate:

Once Y_i, the mole fraction of component i in the vessel vapor space, is known, the VOC or air toxic emission rate may be easily calculated by multiplying Y_i by the vessel fill rate (which equals the gas displacement rate) and converting this volumetric rate to a mass emission using equation (7).

4. Vessel Heating

When a process vessel partially filled with a VOC or a material containing a VOC is heated, the gas and vapors in the headspace expand and are discharged from the vent. An estimate of the emissions in the uncontrolled vent stream from such an event can be calculated based on application of the Ideal Gas Law and on vapor-liquid equilibrium principles.

The basis of the calculation is that the moles of gas displaced from a vessel are a result of the expansion of the noncondensible gas upon heating, and an increase in the VOC vapor pressure. The assumptions made for the calculations which follow are (1) atmospheric pressure of 760 mmHg; and, (2) the displaced gas is always saturated with VOC vapor in equilibrium with the liquid mixture.

The initial pressure of the gas (noncondensible) in the vessel is given by:

$$Pa_1 = 760 - \sum (P_i)_{T1} \tag{11}$$

where:

Pa_1 = initial partial pressure of gas in vessel headspace, mmHg, and
$(P_i)_{T1}$ = initial partial pressure of each VOC in vessel headspace, mmHg, at the initial temperature (T_1).

The choice of formula to calculate P_i depends on which vapor-liquid equilibrium assumption is chosen (as discussed in Section 3 of this Appendix). If the VOC species behaves "ideally" in the system under consideration, then Raoult's Law holds and

$$(P_i)_{T1} = (P_i^{\circ})_{T1} X_i \tag{12}$$

where:

$(P_i^*)_{T1} =$ vapor pressure of each compound at specified temperature, T_1, and

X_i = mole fraction of each compound in the liquid mixture.

If the VOC in question is present in very dilute concentrations in the liquid, then Henry's Law gives a reasonable estimate of the compound partial pressure if the empirically determined constant is available:

$$(P_i)_{T1} = (H_i)_{T1} X_i \qquad (13)$$

where:

H_i = Henry's Law Constant at T_1 in consistent units (atm/mole fractions); and

X_i = Mole fraction of each compound in the liquid mixture.

Note: If neither Raoult's Law nor Henry's Law is considered to be valid for the compound mixture being considered, a more complex procedure, beyond the scope of this document, must be used. Commercial computer programs are available to simplify the task of calculating vapor-liquid equilibria for nonideal mixtures.

The calculation of P_i is repeated at the final temperature conditions, T_2; and the final partial pressure of the gas in the vessel is calculated:

$$Pa_2 = 760 - \Sigma (P_i)_{T2} \qquad (14)$$

By application of the Ideal Gas Law, the moles of gas displaced is represented by:

$$\Delta \eta = \frac{V}{R}\left[\left(\frac{Pa_1}{T_1} \right) - \left(\frac{Pa_2}{T_2} \right) \right] \qquad (15)$$

where:

$\Delta \eta$ = number of lb-moles of gas displaced;

V = volume of free space in the vessel, ft^3;

R   =   Gas Law constant, 998.9 mmHg ft³/lb-moles °K;

Pa_1 =   initial gas pressure in the vessel, mmHg;

Pa_2 =   final gas pressure, mmHg;

T_1 =   initial temperature of vessel, K; and

T_2 =   final temperature of vessel, K.

The concentration of the VOC in the gas displaced at the beginning of the event is calculated assuming equilibrium at the initial vessel temperature. The final concentration of the VOC in the final amount of air displaced is calculated assuming equilibrium at the final vessel temperature. The VOC concentration in the displaced gas may be approximated by assuming it is equal to the average of the initial and final values. The number of moles of VOC displaced is equal to the moles of gas displaced times the average VOC mole fraction, as follows:

$$\eta_s = \frac{\dfrac{\Sigma \left(P_i\right)_{T_1}}{760 - \Sigma \left(P_i\right)_{T_1}} + \dfrac{\Sigma \left(P_i\right)_{T_2}}{760 - \Sigma \left(P_i\right)_{T_2}}}{2} \times \Delta\eta \tag{16}$$

where:

η_s =   lb-moles of VOC vapor displaced from the vessel being heated up.

The mass of VOC vented can be calculated by multiplying the number of moles by the molecular weight. The reader should note that, at the boiling point of the VOC, this equation goes to infinity. In a physical sense, the vessel vapor space is filled entirely with VOC during boiling; the rate of release of VOC is therefore equal to the total flow of VOC out of the kettle. Therefore, this equation is not valid at the boiling point of the VOC.

     5.   Gas Evolution

When a gas is generated as the result of a chemical reaction, emissions may be calculated by assuming that the gas is saturated with any VOCs that are in contact with it at the exit temperature. Emission calculations are analogous to the filled vessel purging calculations and are calculated using the following formula to first calculate the rate of gas displaced:

$$V_t = V_1 \left[\frac{P_T}{P_T - \Sigma (P_i X_i)} \right] \tag{17}$$

where:

V_1 =   initial volumetric rate of noncondensible gas evolution

| P_T | = | vessel pressure |
| $\Sigma (P_iX_i)$ | = | sum of the products of the vapor pressure and the mole fraction of each VOC at the exit temperature |

Once V_2 is known, it can be substituted into Equation (7) to calculate the emission rate.

6.   Sparging

Sparging is the subsurface introduction of a gas (typically nitrogen or other inert gas) intended to remove by selective volatilization (stripping) a more volatile minor component from a liquid mixture of predominantly less volatile material. Common applications of sparging are the removal of trace quantities of water or volatile organic solvent from a low volatility (high boiling point) resin. The removal of low concentrations of organic solvents from wastewater also may be achieved using air sparging.

Sparging is a semibatch operation. The sparge tank is filled or discharged on a batch basis, while the gas is fed continuously at a steady flow rate for the duration of the sparge cycle. The subsurface sparger is designed to develop a mass of small diameter bubbles. The tank may be agitated as well in order to produce fine bubbles and increase the bubble residence time. These design features are intended to increase contact efficiency.

Utilizing fundamental chemical engineering principles and empirical correlations published in the literature it is possible to calculate the mass transfer coefficients encountered in sparging applications. The transfer rate of the component being stripped out is a function of temperature, composition, liquid diffusivity, gas rate and agitator power (which determine bubble size), and tank geometry (which, along with agitation power, determines residence time).

For the calculation of equilibrium concentration of VOC in the exiting sparge gas the earlier discussion of Raoult's Law and Henry's Law applies. For simple sparging (low viscosity fluids; no solids) vapor concentration may approach 100 percent of the calculated equilibrium value. For complex sparging, an empirically determined lower value may need to be used.

Unlike continuous flow vapor-liquid separation processes, with batchwise sparging it is not possible to write a series of simple analytical equations which define the outlet gas concentration as a function of inlet concentration and thermodynamic properties of the compounds. This is because the liquid flow rate is zero and the composition changes with time. The problem of estimating the gas composition (hence, VOC emission rate) at any time during the sparge cycle, or of determining the amount of sparge gas and sparge item required to achieve a certain concentration reduction, can, however, be

solved using simple numerical integration. One chooses a small time increment, one minute, for example, over which to calculate the gas flow and composition, making the simplifying assumption that the liquid composition does not change. From the inlet gas concentration (most likely zero) and the saturated exit gas concentration, the amount of volatile removed from the bulk liquid can be calculated, and a new estimate made for the liquid composition. The calculation of the vapor composition for the next item "slice" will be made based on this new liquid composition value. The cumulative quantity of volatile removed is used for subsequent estimates of the liquid composition.

A graphical representation of the vapor or liquid composition as a function of sparge time has a characteristic hyperbolic shape where the composition is asymptotic to zero. The initial composition is high, as is the stripping rate, because the mass transfer is a function of the composition driving force. The final composition is low, but a long stripping time is required to achieve a small decrease in composition because the driving force is also very low. An example sparging volatilization calculation follows:

Example: A 1,000-gal tank of wastewater containing a 0.025 wt% toluene is to be air sparged to remove the toluene to a concentration level of less than 20 ppb (by weight) to permit discharge to a municipal sewer system. Ambient air is to be used; the design temperature is 20°C. Toluene-water vapor-liquid equilibrium at 20°C can be approximated using a Henry's Law constant of 370 atm.

Solution: Use 1 minute time slices, assume a sparge rate, calculate time required to achieve concentration objective, adjust sparge rate until reasonable cycle time is calculated. Because of standard geometry of 1,000-gal tank, and modest gas rates, 100 percent of equilibrium concentration can be assumed. Table 1 summarizes the results of the calculations made using a personal computer spreadsheet program. With 75 acfm of sparge gas, the desired concentration of 20 ppb toluene is achieved in 55 minutes of sparging. The table clearly shows that the bulk of the VOC is removed during the early part of the cycle: one-half of the total toluene is removed in the first 3 minutes, and 90 percent is removed after 13 minutes.

7.   Batch Pressure Filtration

Pressure filtration of nonaqueous, volatile, flammable, or hazardous slurries is typically conducted in a closed vessel. Generally, VOCs are not emitted during the filtration step, as there is no venting from the process vessel. However, during the gas blowing (cake-drying) step of the cycle, or during pressure release prior to cake discharge, venting occurs and there is potential for VOC emissions.

The gas blowing step is intended to accomplish some preliminary cake drying by evaporating some of the liquid filtrate present in the filter cake. This operation is roughly equivalent to the constant drying-rate period of a dryer's operation except that heated gas is not used (except in the case of some special purpose equipment where

heated gas is, in fact, used). The blowing gas follows the same flow path as the filtrate, so that it could be vented through the receiving tank.

Table 1

Sparging Volatilization

Table 1

(Continued)

	x-bulk	y-exit	#mols out	cum out	new x-b	wt fr	Percent Removal
0	0.000048	0.018090	0.003521	0.003521	0.000041	2.11E-04	15.580%
1	0.000041	0.015271	0.002972	0.006494	0.000034	1.78E-04	28.733%
2	0.000034	0.012892	0.002509	0.009003	0.000029	1.50E-04	39.837%
3	0.000029	0.010883	0.002118	0.011122	0.000024	1.27E-04	49.210%
4	0.000024	0.009188	0.001788	0.012910	0.000020	1.07E-04	57.123%
5	0.000020	0.007756	0.001509	0.014420	0.000017	9.05E-05	63.804%
6	0.000017	0.006548	0.001274	0.015695	0.000014	7.64E-05	69.443%
7	0.000014	0.005527	0.001076	0.016771	0.000012	6.45E-05	74.204%
8	0.000012	0.004666	0.000908	0.017679	0.000010	5.44E-05	78.223%
9	0.000010	0.003939	0.000766	0.018446	0.000008	4.60E-05	81.616%
10	0.000008	0.003325	0.000647	0.019093	0.000007	3.88E-05	84.480%
11	0.000007	0.002807	0.000546	0.019640	0.000006	3.28E-05	86.898%
12	0.000006	0.002370	0.000461	0.020101	0.000005	2.77E-05	88.939%
13	0.000005	0.002000	0.000389	0.020491	0.000004	2.33E-05	90.663%
14	0.000004	0.001689	0.000328	0.020819	0.000003	1.97E-05	92.118%
15	0.000003	0.001425	0.000277	0.021097	0.000003	1.66E-05	93.346%
16	0.000003	0.001203	0.000234	0.021331	0.000002	1.40E-05	94.382%
17	0.000002	0.001016	0.000197	0.021529	0.000002	1.19E-05	95.250%
18	0.000002	0.000857	0.000166	0.021696	0.000001	1.00E-05	95.996%
19	0.000001	0.000724	0.000140	0.021837	0.000001	8.45E-06	96.620%
20	0.000001	0.000611	0.000119	0.021956	0.000001	7.13E-06	97.147%
21	0.000001	0.000516	0.000100	0.022057	0.000001	6.02E-06	97.591%
22	0.000001	0.000435	0.000084	0.022141	9.94E-07	5.08E-06	97.967%
23	9.94E-07	0.000367	0.000071	0.022213	8.39E-07	4.29E-06	98.283%
24	8.39E-07	0.000310	0.000060	0.022273	7.09E-07	3.62E-06	98.551%
25	7.09E-07	0.000262	0.000051	0.022324	5.98E-07	3.06E-06	98.777%
26	5.98E-07	0.000221	0.000043	0.022368	5.05E-07	2.58E-06	98.967%
27	5.05E-07	0.000186	0.000036	0.022404	4.26E-07	2.18E-06	99.128%
28	4.26E-07	0.000157	0.000030	0.022435	3.60E-07	1.84E-06	99.264%
29	3.60E-07	0.000133	0.000025	0.022461	3.04E-07	1.55E-06	99.379%
30	3.04E-07	0.000112	0.000021	0.022482	2.56E-07	1.31E-06	99.475%
31	2.56E-07	0.000094	0.000018	0.022501	2.17E-07	1.11E-06	99.557%
32	2.17E-07	0.000080	0.000015	0.022516	1.83E-07	9.35E-07	99.626%
33	1.83E-07	0.000067	0.000013	0.022530	1.54E-07	7.89E-07	99.684%
34	1.54E-07	0.000057	0.000011	0.022541	1.30E-07	6.66E-07	99.734%

Table 1

(Continued)

	x-bulk	y-exit	#mols out	cum out	new x-b	wt fr	Percent Removal
51	8.67E-09	0.000003	0.0000000	0.022598	7.32E-09	3.74E-08	99.985%
52	7.32E-09	0.000002	.000000	0.022598	6.18E-09	3.16E-08	99.987%
53	6.18E-09	0.000002	0.0000000	0.022599	5.21E-09	2.67E-08	99.989%
54	5.21E-09	0.000001	.000000	0.022599	4.40E-09	2.25E-08	99.991%
55	4.40E-09	0.000001	0.0000000	0.022599	3.72E-09	1.90E-08	99.992%
56	3.72E-09	0.000001	.000000	0.022600	3.14E-09	1.60E-08	99.994%
57	3.14E-09	0.000001	0.0000000	0.022600	2.65E-09	1.35E-08	99.995%
58	2.65E-09	0.000000	.000000	0.022600	2.24E-09	1.14E-08	99.995%
59	2.24E-09	0.000000	0.0000000	0.022600	1.89E-09	9.65E-09	99.996%
60	1.89E-09	0.000000	.000000	0.0226000	1.59E-09	8.15E-09	99.997%
61	1.59E-09	0.000000	0.0000000	.022600	1.35E-09	6.88E-09	99.997%
62	1.35E-09	0.000000	.000000	0.022600	1.14E-09	5.81E-09	99.998%
63	1.14E-09	0.000000	0.0000000	0.022601	9.59E-10	4.90E-09	99.998%
64	9.59E-10	0.000000	.0000000.	0.022601	8.09E-10	4.14E-09	99.998%
65	8.09E-10	0.000000	000000	0.022601	6.83E-10	3.49E-09	99.999%
66	6.83E-10	0.000000	0.0000000	0.022601	5.77E-10	2.95E-09	99.999%
67	5.77E-10	0.000000	.000000	0.022601	4.87E-10	2.49E-09	99.999%
68	4.87E-10	0.000000	0.0000000	0.022601	4.11E-10	2.10E-09	99.999%
69	4.11E-10	0.000000	.000000	0.022601	3.47E-10	1.77E-09	99.999%
70	3.47E-10	0.000000	0.000000	0.022601	2.93E-10	1.50E-09	99.999%

i. Filter Cake Purging. The emission rate in the vented purge/blowing gas can be calculated if the cake conditions at the start and end of this portion of the cycle are known. The filtrate will be evaporated at approximately a constant rate. Assuming that the filtrate is 100% VOC, the emissions rate is simply:

$$ER = \frac{W(X_i - X_f)}{t} \qquad (18)$$

where:

W	=	the dry weight of a batch of filter cake;
X_i	=	the weight fraction of filtrate at the start of the gas-blowing step;
X_f	=	the weight fraction of filtrate at the end of the gas-blowing step;
t	=	elapsed time of gas blowing; and
ER	=	emission rate in weight per unit time.

However, one key piece of data required for the above calculations, namely the filtrate content of the cake before the gas blowing, is not usually available. Therefore, this methodology is of only limited utility.

Since the blowing gas causes the VOCs in the filtrate to evaporate, the gas stream is partially saturated with vapor, and approaches vapor-liquid equilibrium as a limit. An assumption of the attained percent saturation enables the calculation of an emission rate.

ii. Depressurization. Prior to opening a batch pressure filter for solids discharges, the pressure must be relieved. In the case of a filter design utilizing a closed vessel, there is some compressed gas in the vapor space which will have some degree of vapor saturation of VOC from the filtrate. Upon depressurization, a fraction of the noncondensible gas along with the VOC vapor will be vented. The estimation of the emission rate from a depressurization event is a straightforward application of the Ideal Gas Law if certain simplifying assumptions are made.

If the vessel has been under pressure for some time during the filter cycle, and no additional noncondensible gas has been added, then it is reasonable to assume that the gas is saturated with the VOC vapor at the vessel temperature. To simplify the calculations, one assumes that the pressure decreases linearly with time once

depressurization has begun, and that the composition of the gas/vapor mixture is always saturated with VOC vapor through the end of the depressurization. The estimation of the emission rate proceeds according to the following steps:

1.   Calculate the mole fraction of each VOC vapor species initially present in the vessel at the end of the depressurization.

$$Y_i = \frac{X_i P_i}{P_1} \tag{19}$$

where:

P_i	=	vapor pressure of each VOC component i;
P_1	=	initial pressure of the process vessel in units consistent with P_i calculations;
X_i	=	mole fraction of component i in liquid; and
Y_i	=	mole fraction of component i initially in the vapor.

2.   The moles of VOC initially in the vessel are then calculated using the Ideal Gas Law as follows:

$$n_{voc} = \frac{(Y_{voc})\,(V)\,(P_1)}{R\,T} \tag{20}$$

where:

Y_{VOC}	=	mole fraction of VOC (the sum of the individual VOC fractions, ΣY_i);
V	=	free volume in the vessel being depressurized;
P_1	=	initial vessel pressure;
R	=	ideal gas constant; and
T	=	vessel temperature, absolute units.

3.   The moles of noncondensible gas present initially in the vessel are calculated as follows:

$$n_1 = \frac{V P_{nc_1}}{RT} \tag{21}$$

where:

V = free volume in the vessel being depressurized;

P_{NC1} = initial partial pressure of the noncondensible gas, $P_1 - \Sigma P_i$;

R = gas law constant; and

T = temperature, absolute units.

4. At the beginning of the depressurization, there are more moles of noncondensible gas in the vessel relative to the moles of VOC in the vessel than at the end of depressurization. At the beginning of the depressurization, there are:

$$\frac{n_{VOC}}{n_1} \quad \text{moles of VOC to noncondensables}$$

5. At the end of depressurization, there are:

$$\frac{n_{VOC}}{n_2} \quad \text{moles of VOC to noncondensables}$$

where:

$$n_2 = \frac{V\, P_{NC_2}}{RT} \qquad\qquad (22)$$

where:

V = free volume in the vessel being depressurized;

P_{NC2} = final partial pressure of the noncondensible gas, $P_2 - \Sigma X_i P_i$;

R = gas law constant; and

T = temperature, absolute.

6. The moles of VOC for the duration of the depressurization may be calculated by taking an approximation of the average ratio of moles of VOC to moles of noncondensibles and multiplying by the total moles of noncondensibles released during the depressurization, or:

$$\frac{\left(\dfrac{n_{VOC}}{n_1} + \dfrac{n_{VOC}}{n_2}\right)}{2} \left[n_2 - n_1\right] = N_{VOC} \tag{23}$$

where:

N_{VOC} = moles of VOC emitted.

7. The moles of VOC emitted can be converted to a mass rate using the following equation:

$$\frac{N_{VOC} \times MW_{VOC}}{t} = ER_{VOC} \tag{24}$$

where:

ER_{VOC} = emission rate of the VOC;
MW_{VOC} = molecular weight of the VOC; and
t = time of depressurization.

8. Emissions from Vacuum Generating Equipment

Steam ejectors and vacuum pumps are used to pull vacuums on vessels and can be sources of VOC and air toxic emissions. Both come in contact with a stream of gas that potentially contains pollutants. A steam ejector consists essentially of a steam nozzle that produces a high-velocity jet across a suction chamber connected to the vessel being evacuated. The gas from the vessel is entrained into the motive steam as it passes across the suction chamber. Both gas and steam are usually routed to a condenser.

Conventional (mechanical-type) vacuum pumps use a high boiling point oil to lubricate the moving parts. The VOCs which are present in the gas on the suction side may be

partially condensed in the elevated pressure inside the vacuum pump. This reduces the amount of VOC emitted in the gas discharge from the pump, but causes contamination (reduced viscosity) of the pump oil. For this reason, if a significant amount of VOC is expected in the gas being evacuated, a liquid ring vacuum pump may be selected.

In a liquid ring vacuum pump, the vacuum is created by the rotating motion of a slug of seal fluid inside the pump casing. The seal fluid is in intimate contact with the gas and VOC being evacuated. A portion of the seal fluid is ejected with the pump discharge, so a system for seal fluid recycle and makeup is required.

Because the seal fluid is in contact with the gas/VOC mixture, mass and heat transfer can occur inside the pump. The emissions from a liquid ring vacuum pump are, therefore, a function of the seal fluid temperature and composition, as well as the inlet gas composition. For purposes of calculation one may assume that the exiting gas is in equilibrium with the seal fluid. The seal fluid must be chosen to be compatible with the gas/VOC being evacuated. In some cases, the seal fluid itself is a VOC and equilibrium with the exiting gas may result in an increase in VOC level from that in the suction side. In other cases, the seal fluid can act to reduce the VOC level of the gas stream by absorbing (or condensing, in the case of a cooled seal fluid system) some of the VOC in the gas being evacuated.

> i.   Emission Estimation. Emissions from vacuum systems originate from two distinct sources: 1) the first is the gas at the vacuum system discharge, 2) the second is the seal fluid or motive steam. Calculating emissions from the gaseous discharge of systems that serve to induce vacuums on equipment involves the estimation of the amount of air that leaks into the equipment because of the pressure differential between the inside and outside of the vessel. Once this air leakage rate is known, the rate of VOC emissions may be calculated by knowing the vacuum system discharge outlet temperature and pressure.

The air leakage rate for the equipment may be estimated from the following equations, which correspond to the leakage created by metal porosity and cracks and leakage resulting from seals and components in a system for various vacuum pressure ranges:

     1.   Leakage from metal porosity and cracks

(For $1 \le P \le 10$ mmHg)	$W = 0.026\, P^{0.34}V^{0.60}$	(25)
(For $10 \le P \le 100$ mmHg)	$W = 0.032\, P^{0.26}V^{0.60}D$	(26)
(For $100 \le P \le 760$ mmHg)	$W = 0.106\, V^{0.60}$	(27)

where:

P =   system operating pressure, mmHg;

V =   volume, ft^3; and

W =   air leakage resulting from metal porosities and cracks along weld lines, lb/hr.

     2.   Leakage from seals and components

(For $1 \le P \le 10$ mmHg)	$w = \pi D\theta P^{0.34}$	(28)
(For $10 \le P \le 100$ mmHg)	$w = 1.20\, \pi D\theta P^{0.26}$	(29)
(For $100 \le P \le 760$ mmHg)	$w = 3.98\, \pi D\theta$	(30)

where:

D =   sealed diameter, inches;

w =   acceptable air leakage rate assigned to a system component, lb/yr; and

θ =   specific leakage rate for components, lb/hr/in (presented in Table A-5 of Appendix A).

     3.   The total air leakage rate, L_a, in lb/hr, is merely the sum of the two components W and w.

$$L_a = W + w \tag{31}$$

Once the air leakage rate is known, the VOC emission rate, in lb/hr, may be calculated using the following equation from the 1978 Pharmaceuticals CTG:[4]

$$SE = MW_{VOC}\, \frac{L_a}{29} \left(\frac{P_{system}}{P_{system} - P_i} - 1 \right) \tag{32}$$

where:

SE   =   rate of VOC emission, in lb/hr;

MW_{VOC} =   molecular weight of VOC, lb/lbmole;

P_{system} =   absolute pressure of receiving vessel or ejector outlet conditions, if

		there is no receiver;
P_i	=	vapor pressure of the VOC at the receiver temperature, in mmHg;
L_a	=	total air leak rate in the system, lb/hr; and
29	=	molecular weight of air, lb/lbmole.

Calculating emissions from seal fluid or motive steam is analogous to the calculations of VOC emissions from other sources of wastewater, which is discussed below.

b.   Evaporative Losses From Wastewater

Evaporative losses from wastewater that is contaminated with VOCs has been examined in detail, but currently is not included in this Appendix. Several publications are available to aid the readers in calculating emissions from wastewater treatment systems which include surface impoundments, lagoons, and basins.[5,6,7]

c.   Storage Tank Emissions

In general, emissions of VOCs from storage tank working and breathing losses appear to be no different for continuous processes than they are for batch processes. Both types of losses usually are calculated using EPA-derived storage tank loss equations for three types of storage tanks: fixed roof, external floating roof, and internal floating roof. Fixed roof and horizontal pressure tanks appear to be the most common storage vessels used in batch processing. Estimation equations for these tank types and a detailed explanation of their use, may be found in an EPA reference.[8]

d.   Equipment Leaks

The calculation of emissions of VOCs from leaking process line components such as valves, pump seals, flanges, and sampling connections is no different for continuous processes than it is for batch processes. Emissions tend to be lower because the amount of time that components are actually in VOC service is less for batch processes than for continuous processes.

In the event that no other specific data is available, equipment leak emissions may be estimated using the equipment leak factors derived for the Synthetic Organic Chemical Manufacturing Industry (SOCMI). These factors are readily available, and are included in Table 2. It is also possible to develop unit-specific emission estimates according to an accepted EPA protocol. The methodology for developing a specific emission estimate for leaking components is contained in another reference.[10]

Table 2

Average Emission Factors for Fugitive Emissions in SOCMI[a]

Equipment Component	"Average" SOCMI factors, Kg/h/source
Pump seals	
Light liquid	0.0199
Heavy liquid	0.00862
Valves	
Gas	0.00597
Light liquid	0.00403
Heavy liquid	0.00023
Compressor seals	0.228
Safety relief valves--gas	0.104
Flanges	0.00183
Open-ended lines	0.0017
Sampling connections	0.0150

[a]These factors are appropriate for estimating emissions when no other data (i.e., leakage rates) are available.

Source: EPA-953/R-93-026. June 1993.

e.   <u>References</u>

1.   McCabe, W., and J. Smith. Unit Operations of Chemical Engineering, Third Edition. 1976.

2.   Ryan, J.L., and S. Croll. Selecting Vacuum Systems. Chemical Engineering. 88:78. December 14, 1981.

3.   Blakely, P. and G. Orlando. Using Inert Gasses for Purging, Blanketing, and Transfer. Chemical Engineering. 91:97-102. May 28, 1984.

4.   EPA-450/2-78-029. Control of Volatile Organic Emissions from Manufacture of Synthesized Pharmaceutical Products. December 1978.

5.   EPA-450/3-87-026. Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) Air Emission Models.

6.   Wastewater and Wastes Enabling Document. Version 1.0, July 1992.

7.   Industrial Wastewater Volatile Organic Compound Emissions - Background Information for BACT/LAER Determinations.

8.   AP-42 Compilation of Air Pollution Emission Factors, Chapter 12.

9.   EPA-453/R-93-026, Protocol for Equipment Leak Emission Estimates. June 1993.

10.   EPA-450/3-88-010, Protocol for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP. October 1988.